


# Diamonds Put the Pressure

*Novel capabilities in high-pressure pressures lead to dramatic changes*



Livermore researchers have developed two new devices for studying materials under extremely high pressures. (above) The dynamic diamond anvil cell (dDAC) compresses micrometer-size samples between two brilliant-cut diamonds. (right) The moissanite anvil cell (MAC) uses larger moissanite (silicon carbide) anvils instead of diamond, allowing researchers to examine millimeter-size samples.

# on Materials

*science are revealing how extreme  
in material microstructures and phases.*

**I**n nature, matter sometimes undergoes dramatic transformations that affect not only the state, or phase, of a material (changing it from gas to liquid to solid) but also its microscopic structure, or microstructure. For instance, when liquid water is boiled, it becomes a gas, but when frozen, it crystallizes. Even then, its microstructure can range from coarse-grained, as in a hard ice cube, to fine-grained, as in a “soft” Popsicle.

Just as temperature can change the state of matter, applying pressure can modify it as well. For example, one method to produce synthetic diamond uses high pressure and high temperature to transform carbon from the hexagonal structure of graphite into the hard diamond structure.

To examine materials under extreme pressures, Livermore scientists often use a device called a diamond anvil cell (DAC). (See *S&TR*, December 2004, pp. 4–11.) This small mechanical press forces together the tiny, flat tips of two flawless diamond anvils. As the diamond tips slowly compress a microgram sample of a material, they generate a fixed-pressure environment similar to that deep

inside Earth’s core, where pressure is up to 360 gigapascals (GPa), or 3.6 million times atmospheric pressure.

The material’s phase and microstructure are affected not only by the amount of pressure but also by the rate at which it is applied. Traditional DACs, however, do not allow researchers to change the speed of compression with any precision during an experiment. To study a material’s response to different compression rates, a team of Livermore researchers developed a new generation of DAC devices, called dynamic DACs (dDACs). With dDACs, scientists can control the compression rate by changing how quickly the anvils squeeze together or contract. “By varying the pressure, we can study how different rates induce microstructural changes in materials,” says Livermore physicist William Evans, who works in the Physical and Life Sciences Directorate and leads the dDAC team.

Another new device, called the moissanite anvil cell (MAC), allows researchers to examine larger material samples than they can study with DACs and dDACs. In a MAC, moissanite (silicon

carbide) anvils replace the diamond anvils in a DAC.

Together, the Livermore-developed technologies will improve scientific understanding of the processes that occur at extremely high pressures and temperatures, such as in a meteor impact, during a high-explosive detonation, or deep within a planet’s interior. Using these devices, researchers can develop advanced materials for new technologies and replicate specific phases and microstructures of synthetic superhard materials, such as diamond and cubic boron nitride, both of which are widely used as abrasives. Experiments at the Laboratory and the High Pressure Collaborative Access Team facility near Chicago, Illinois, are helping the team better understand how materials change at the microstructural level under a broad range of temperatures and pressures. (See the box on p. 6.)

## **Bridging the Knowledge Gap**

According to Evans, high-pressure experimental science has traditionally been split between two approaches—dynamic and static. In dynamic, or shock,



experiments, a projectile accelerated by a laser or a gas- or explosive-driven gun impacts a sample. Scientists then measure the resulting wave of pressure and the speed of material particles accelerated by the impact to gather information about material properties under high pressures.

Shock experiments last no more than a few microseconds and can attain pressures up to several hundred gigapascals. Acquiring

data from these experiments is challenging, however, because the short, single-shot events produce extremely high temperatures, up to several thousand kelvins. Only a few diagnostic techniques can record results in this environment. (See *S&TR*, June 2009, pp. 22–23.)

In contrast, static experiments use opposing anvils to exert a fixed pressure on a material. The maximum pressure

achievable with this method is about 350 GPa, and temperature can range from less than 1 kelvin to a few thousand kelvins. Unlike dynamic experiments, static experiments typically last for several days and have no time limit for data collection. With fixed-pressure systems, a sample can be probed using various noninvasive techniques such as optical spectroscopy, electrical conductivity, and x-ray scattering.

### A High-Tech Facility for High-Pressure Research

Scientists are interested in examining the structural evolution of pressure-induced phase transitions in materials because these processes occur in projectile and meteoritic impacts and can affect planetary models and industrial fabrication techniques. The x-ray capabilities available at the High Pressure Collaborative Access Team (HPCAT) facility allow them to rapidly collect data from diamond anvil cell (DAC) samples under extreme pressures and temperatures.

HPCAT is a multidisciplinary program established in 1998 with funding from the Department of Energy's National Nuclear Security Administration and Office of Basic Energy Sciences to integrate multiple synchrotron x-ray diffraction and x-ray spectroscopy probes

as well as complementary optical and electromagnetic probes. In addition to Livermore, HPCAT members include Carnegie Institution of Washington, Carnegie/Department of Energy Alliance Center, and University of Nevada's High Pressure Science and Engineering Center. The HPCAT facility opened to users in 2002 and is part of Argonne National Laboratory's Advanced Photon Source, located about 50 kilometers southwest of Chicago, Illinois.

"The HPCAT facility is specifically designed for high-pressure experiments with very tightly focused x-ray beams and instrumentation," says Livermore physicist William Evans. "It is the highest performance hard x-ray source in the U.S."

Evans and members of the Laboratory's High Pressure Physics Group are using the HPCAT facility to study phase transformations and the properties of materials over a broad range of pressure and temperature conditions. "The knowledge gained from our research will help us better understand material behavior at high pressures," says Evans. "Our results will provide a robust, high-fidelity experimental basis for predictive models of high-pressure systems including terrestrial structure and processes, planetary bodies, high-energy impacts, and advanced technological manufacturing processes."



The High Pressure Collaborative Access Team is one of many programs operating at Argonne National Laboratory's Advanced Photon Source, shown above. (Photo courtesy of Argonne National Laboratory.)

Dynamic and static experiments are complementary approaches. However, because the two techniques operate at different time scales and within different temperature ranges, their results are difficult to compare directly.

“The dynamic diamond anvil cell bridges the gap between static and dynamic experiments to address questions about how materials and microstructures transform and evolve at high pressures,” says Evans. “Very little has been published from experimental studies of these dynamic, pressure-induced transitions, and we know of no other groups in the world who have made an instrument that performs this way. The dynamic diamond anvil cell is an important advance for studying such a rich area of materials physics.”

### Dynamic Diamond Device

Diamonds are an appealing material for use in anvil cells because they are the hardest known solid and can withstand ultrahigh pressures. In addition, a sample can be viewed through the diamonds and probed by x rays and visible light.

Fabricating a diamond anvil is a multistep process that generally begins with a brilliant-cut, 0.33-carat diamond consisting of 58 facets. The diamond must be free of inclusions or defects that could weaken it under pressure. At 100 GPa and above, diamonds occasionally shatter into dust. “However,” says Evans, “we usually try not to push them to this pressure limit, so we can reuse them multiple times.”

The tip of the diamond is polished until a flat surface, called a culet, is formed, providing a surface on which to place the sample. Although the culet appears round, examination under a microscope reveals that its face is actually an octagon. It takes this shape because the conical section of a cut diamond consists of facets, rather than a smooth cone, and the culet is formed by lopping off the end of the cone. For experiments below 50 GPa, the culet ranges from 0.1 to 0.5 millimeters in

diameter. For experiments above 50 GPa, it can be as small as 0.05 millimeters, and its sides are beveled downward to improve performance.

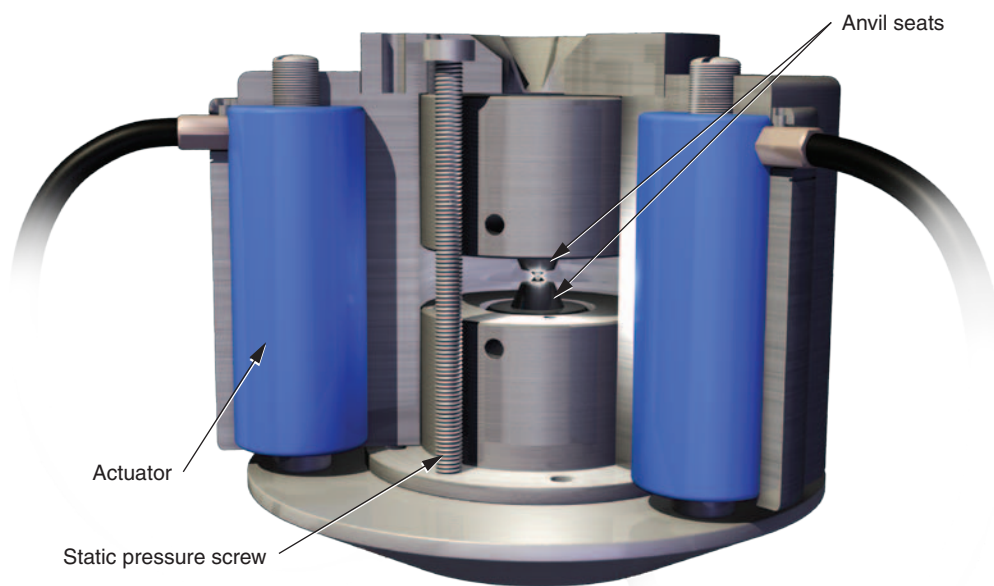
In a DAC, two diamonds are mounted in a cylinder that keeps the anvil tips aligned as the diamonds are driven together. Samples placed between the diamonds are held in place laterally by a gasket. The dDAC device enhances the basic DAC design by incorporating an electromechanical piezoelectric actuator that varies the pressure on the sample. The sample is first compressed under a fixed pressure. The actuator then applies an additional force that is either expansive (contracting) or compressive (squeezing together). “The electronic drive of the piezoelectric actuator permits precise changes in the pressure that we can reproduce multiple times,” says Evans. “In our experiments, we have shifted the pressure by as much as 50 percent of the initial fixed pressure and have achieved compression rates of up to 500 GPa per second, or 5 GPa in 10 milliseconds.”

A typical dDAC sample is about 300 micrometers in diameter, or about 3 times the diameter of a human hair. As the device compresses and decompresses a sample, researchers measure changes in the material’s microstructure and thermodynamic state. A video camera capturing 2,000 frames per second records the pressure-induced melting or freezing of the material.

The dDAC project, which began in 2005, is funded by the Science Campaign of the National Nuclear Security Administration. Key contributors include two former Livermore scientists: Choong-Shik Yoo, now a professor at Washington State University, and Geun Woo Lee, now a researcher at the Korean Research Institute of Standards and Science.

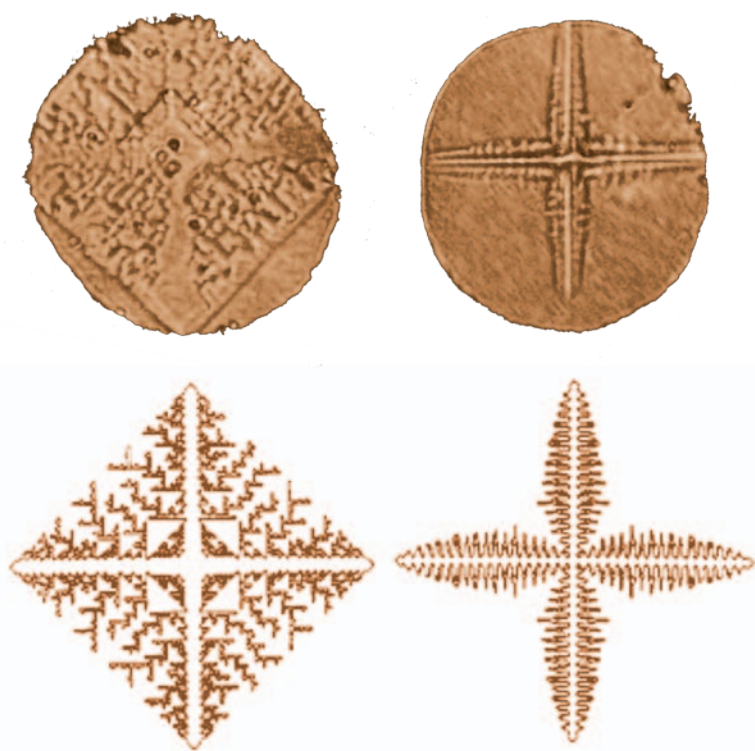
### Crystal-Clear Water

Using the control mechanisms on dDAC, researchers can adjust the pressure and temperature in experiments and thus transform material samples into metastable phases. For example, water that



This diagram shows the setup for a dDAC device. As diamond anvils compress micrometer-size samples, the piezoelectric actuator varies the static pressure, allowing researchers to examine how compression rate affects material behavior. (Rendering by Kwei-Yu Chu.)

Microphotographic images of pressure-induced dendritic crystals (top row) are remarkably similar to the patterns produced in computer simulations of temperature-driven dendritic crystal growth (bottom row).



is supercooled can remain in liquid form at below-freezing temperatures until an external disturbance, such as a vibration or a seed particle, causes the solid ice phase to form.

The dDAC research shows that a material can also be superpressurized and will remain liquid beyond pressures that would typically transform it into a solid. In addition, liquid water can crystallize into unexpected metastable structures that are not observed under atmospheric pressures.

“Using dDAC, we can directly observe pressure-induced crystal growth and study how the compression rate influences morphology and growth mechanisms,” Evans says. “Traditionally, crystal growth has been studied from the thermal perspective by varying the temperature or the cooling rate. The dDAC device permits an analogous approach with pressure.”

In a dDAC study of water, the Livermore team found that different crystallization processes take place depending on the compression rate. At room temperature and thermodynamic

equilibrium, water solidifies at 0.9 GPa into the ice-VI structure (a tetragonal crystal structure in which two of the three crystallographic axes are equal in length, and all are at 90-degree angles). When pressure increases to 2.2 GPa, water transforms to ice-VII (a cubic crystal structure with three axes of equal lengths, all with 90-degree angles). Both of these structures differ from the familiar hexagonal structure of an ice cube at normal atmospheric pressure.

However, when the compression rate is greater than 0.08 GPa per second, water maintains its liquid phase up to 1.8 GPa, well beyond the 0.9-GPa transformation point. Even more surprising, the team found that the supercompressed water crystallized into the ice-VII structure while still in the thermodynamic stability field of ice-VI. “This finding suggests that compression rates may cause other metastable ice phases to form,” says Evans. “Clearly, further investigation is needed to fully understand the phase

transformation and stability of molecular fluids and solids.”

Crystal growth is an area of science where dDAC could make an important contribution, according to Evans. High-speed videos of crystals growing in water showed dramatic changes in the morphology and rate of growth as the compression rate changed. A faceted crystal formed at slow compression. However, when the rate increased to approximately 120 GPa per second, the growth patterns resembled multi-branching, treelike dendrites. Surface instabilities also appeared, which led to extremely rapid crystal growth.

### Sometimes Size Matters

Although many high-pressure studies can be performed with dDACs, the small size of the diamond anvil limits the size of samples that can be examined. “We can’t study large samples with dDACs,” says Livermore geophysicist Dan Farber. “We may only be able to look at a few crystalline grains from a test material. Such small samples aren’t effective if the property we want to study is dependent on grain size.”

To meet this challenge, Farber is leading a team of five researchers in the Laboratory’s Physical and Life Sciences Directorate to develop MACs. The moissanite anvils for a MAC are 6 carats each and can hold samples as large as 3 millimeters in diameter compared with the 0.1- to 0.3-millimeter samples that a dDAC can compress.

Synthetic single-crystal moissanite is an ideal anvil material because of its high hardness and excellent optical properties (for example, it is transparent to visible light). The moissanite crystals used by Farber’s team are manufactured outside the Laboratory at a fraction of the cost for similar-sized diamonds. They are not faceted like the dDAC anvils but are conical, and the culet of the moissanite anvils can be fashioned to a near circle.



MACs can test samples with grain sizes larger than 10 micrometers and materials such as plutonium that are extremely difficult to handle in microscopic sizes. The MAC development project, which began in 2006, is funded by the National Nuclear Security Administration. In one MAC experiment, Farber, Livermore scientist Adam Schwartz, and their colleagues pressurized a sample of plutonium and examined the sample's microstructure using the Laboratory's transmission electron microscope. Results showed different morphologies for a phase of plutonium

formed under high pressure and the same phase formed by reducing temperature.

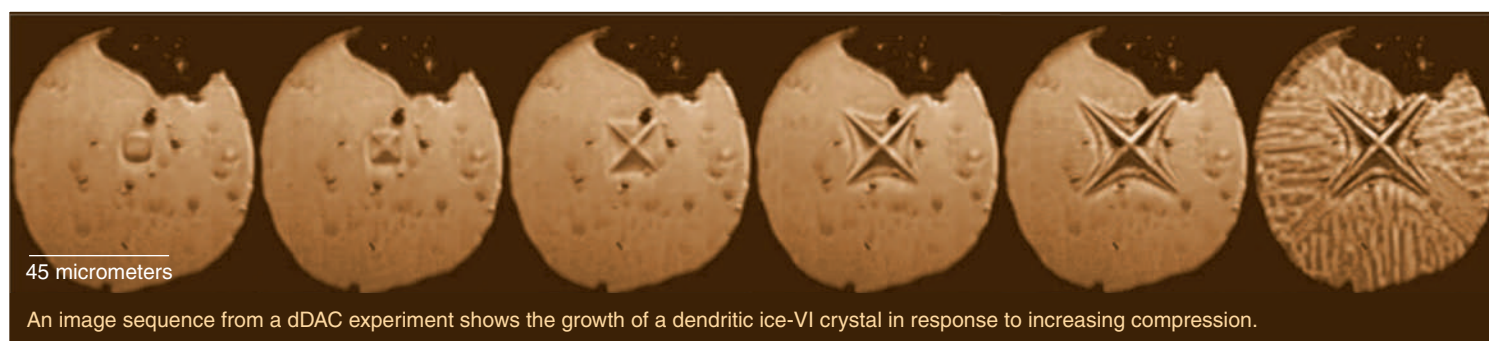
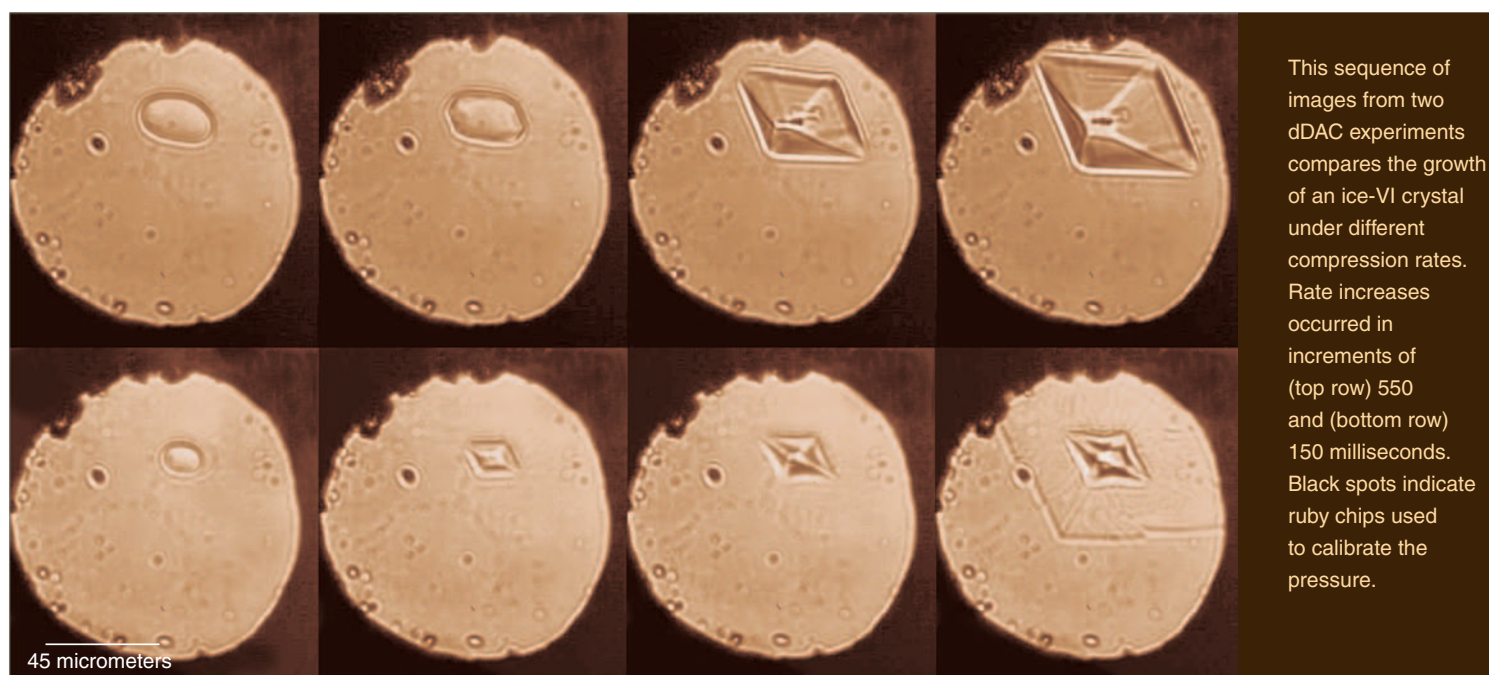
Although MACs are in the same family of research instruments as dDACs, they are not nearly as dynamic. Says Farber, "We can vary the rate of pressure with a MAC but not as quickly as we can with a dDAC." Instead, the team compresses a sample hydrostatically, using a range of pressure-transmitting materials, to create a uniformly pressurized environment that encloses the sample.

In general, MACs cannot withstand pressures as high as those applied by

dDACs. The Livermore MAC device has achieved a maximum pressure of 5 GPa, while diamond anvils can reach nearly 70 times that pressure. "The classic problem is that we can't generate high pressures and temperatures with MACs like we can with dDACs," says Farber. "On the other hand, although we can vary pressures dynamically with dDACs, we can't look at large samples."

### High Potential at High Pressures

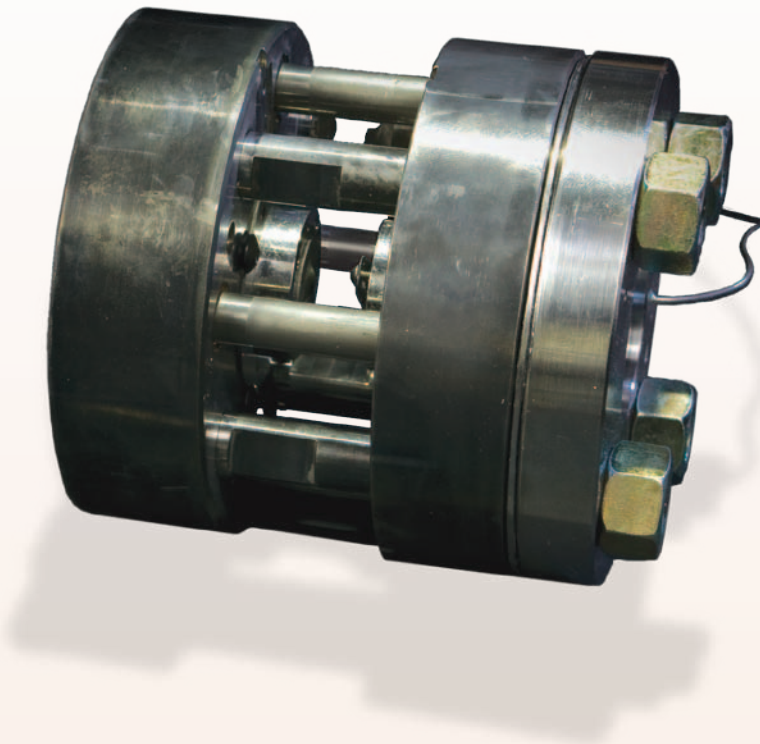
Understanding how material properties change as a function of pressure and



temperature is important to various science and technology efforts. Recent advances in high-pressure science at Livermore provide insights about subsurface planetary dynamics. Modeling the processes that occur at a planet's core cannot proceed without knowledge of material properties

at extreme pressure. In addition, new capabilities in high-pressure manufacturing may allow developers to precisely control microstructure to produce materials that are superhard, provide enhanced structural support, or improve optical communication.

The moissanite anvils for a MAC are 6 carats each and can hold samples up to 3 millimeters in diameter compared with the 0.1- to 0.3-millimeter-diameter samples that a dDAC can compress.



Preliminary studies using dDACs and MACs have already demonstrated significant progress, and according to Evans, this work is just beginning to reveal the potential of the two devices. "In the future, we will address a wide range of topics such as phase transformation kinetics and loading-rate-dependent phenomena," he says.

Farber adds that each technique has its limits. However, he says, "Using both instruments will allow us to investigate material strength and phase transitions in a way that couldn't be done before."

—Kristen Light

**Key Words:** compression rate, crystal growth, dynamic diamond anvil cell (dDAC), high-pressure experiment, material dynamics, moissanite anvil cell (MAC), phase transformation kinetics, static experiment, superhard material.

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